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VOLUME 56, NUMBER 5

A PRELIMINARY STUDY OF CHEMICAL
DENUDATION

BY

FRANK WIGGLESWORTH CLARKE

CHIEF CHEMIST, U. S. GEOLOGICAL SURVEY



(PUBLICATION 1935)

CITY OF WASHINGTON
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A PRELIMINARY STUDY OF CHEMICAL DENUDATION

BY FRANK WIGGLESWORTH CLARKE

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In 1876 the late T. Mellard Reade delivered a remarkable address before the Liverpool Geological Society,¹ which was afterwards separately printed under the title, "Chemical Denudation in Relation to Geological Time." In this address Reade attempted to measure the solvent action of surface waters in England and Wales, and to estimate the amount of dissolved solids annually carried by British rivers to the sea. His conclusion was, in brief, that the annual run-off in England and Wales transported 8,370,630 tons of mineral matter in solution; a quantity which would represent a lowering of the area in question at the rate of one foot in 12,978 years. Evenly distributed, the amount of material so removed from the land amounted to 143.5 tons per square mile of surface, a figure which is surprisingly large. Reade also, from such data as he could obtain, made similar but rough estimates for several European river basins; which, in British tons per square mile, may be tabulated as follows:

Rhone	232.
Thames	149.
Garonne	142.
Seine	97.
Rhine	92.3
Danube	72.7

The average for the entire land surface of the globe he put at 100 tons per square mile, a figure that was not much better than a guess.

About eight years later, in another address before the Liverpool Society, Reade discussed the subject of denudation in the two Americas.² For the Mississippi, on the basis of a single old and imperfect analysis, he computed a solvent lowering of the drainage basin at the rate of 120 tons per square mile per annum and for the Amazon his figure was 50 tons. For the St. Lawrence and the River Plate his figures are less explicit, but the St. Lawrence he considers as having a greater chemical activity per square mile than the Mississippi. His former average of 100 tons for all the river basins of the globe he regarded as confirmed.

¹ Proc. Liverpool Geol. Soc., vol. 8, p. 211, 1876.

² See "The Evolution of Earth Structures," pp. 255-282. London, 1908.

In 1887 Sir John Murray¹ published a careful discussion of the relations between rainfall and run-off for the entire globe, and incidentally, from the average composition of nineteen rivers he estimated that the saline matter annually carried into the ocean amounted to nearly 5,000,000,000 tons. The rivers taken for this estimate were not named, but must have been in great part European. American data were at that time very meager, and, except for the Nile, there was little material to be had relative to the rivers of Africa and Asia. Reade and Murray both were handicapped by the defectiveness of their data; and yet their conclusions were so important that they have since been made the basis of several attempts to compute geological time. These attempts will be considered in due course later. It is now time to revise some of the fundamental figures.

Within the past year, 1909, two noteworthy reports have been published by the United States Geological Survey.² In one of them Dole and Stabler have summarized a great number of observations upon the discharge, drainage areas and salinity of many American rivers, and in the other Dole has given detailed analyses of the waters east of the hundredth meridian. These analyses are numbered by thousands, and in each case the composition of a river water represents the average composition during an entire year. For example, the water of the Mississippi, taken just above New Orleans,³ was collected daily. Each week the seven samples were mixed and analyzed, and this was repeated regularly during the year. The average of the fifty-two weekly composites gave the mean composition of the river; and, combined with the known discharge, the amount of dissolved matter contributed annually by the entire drainage basin of the Mississippi to the Gulf of Mexico. With evidence of this kind the problem of chemical denudation can now be attacked systematically; and to do so is the purpose of this paper.

First of all, let us try to determine the average composition of the inorganic matter held in solution by river waters, taking into account as far as possible the entire surface of our globe. This is a subject of fundamental importance; for upon its details the estimates of geological time, to which reference has already been made, must be based. For the rivers of the United States the material, although not exhaustive, is adequate; for Europe a fair average can be computed; but beyond these areas the evidence is still very imperfect. Something, however, can be done even with the scanty data which now exist; by comparing the analyses of Asiatic or African waters with those of similar areas elsewhere. The com-

¹ Scottish Geographical Magazine, vol. 8, p. 65, 1887.

² Water-Supply Papers 284 and 236.

³ The river was also studied with great thoroughness at several other points, and so too were its more important tributaries.

position of a river water shows marked climatic features, and the magnitude of the load carried is affected in the same way. In the Temperate Zone, alternations of freezing and thawing tend to break up the rocks and so to render them more easily decomposed by percolating waters. With even moderate humidity the activity of the waters is great, and large amounts of material are transported by them. The rivers of Europe and of the eastern United States are marked by more than the average salinity of flowing waters, and estimates based upon them exclusively are sure to be excessive. In an arid region, although salinity may be high, the run-off is small, and much of an ostensible drainage area will contribute little or nothing to the mineral matter of a stream. Arctic rivers flow to a considerable extent over tundra, which is frozen during the greater part of the year. They, therefore, have comparatively small influence in rock solution, and much of their flow must be mere surface run-off. So also tropical rivers like the Amazon carry relatively light loads in solution, for their courses are largely through swamps and forests where the soil, un replenished by fresh rock decomposition, has been leached for centuries and so deprived in great part of its soluble matter.

To illustrate some of these differences in the composition of stream waters a few typical examples may be taken. The analyses represent, in ionic form, the percentage composition of the dissolved mineral matter, and under the caption of *denudation factor* I give the number of metric tons annually removed in solution from each square mile of a drainage basin. The following waters have been chosen for this purpose:

- A. The St. Lawrence at Ogdensburg. Annual average as given by Dole, the denudation factor by Dole and Stabler.¹
- B. The Mississippi at New Orleans. Annual average; Dole and Stabler. Analyses by J. L. Porter.
- C. The Rio Grande at Laredo, Texas. Annual average as given by Dole from analyses by W. H. Heileman. Denudation factor from Dole and Stabler.
- D. The Colorado at Yuma. Mean annual composition as given by Forbes and Skinner. Bull. 44, Arizona Agric. Exper. Station, 1902. Denudation factor by Dole and Stabler.
- E. The Amazon. A single analysis by P. F. Frankland, used by Reade. Two analyses by Katzer give lower salinities, and, therefore, a smaller transport of material. For the total discharge of the river I have taken the data given by Murray in the memoir already cited.

¹ Dole and Stabler's figures for denudation are given in tons of 2000 lbs. They are here reduced to metric tons of 2205 lbs. The analyses are recalculated to two decimal places.

F. The Uruguay. Mean of two analyses by Kyle and Schoeller.¹ Denudation computed from Murray's figures for the discharge and drainage area.

G. The Nile. Annual average as shown by Letheby's analyses.² Drainage area from Murray. Total dissolved matter, 20,772,400 metric tons per annum according to Chélu.³

	A.	B.	C.	D.	E.	F.	G.
CO ₂	45.69	35.21	11.55	13.02	34.75	22.91	36.50
SO ₄	9.08	15.36	30.09	28.61	7.37	5.02	17.44
Cl	5.82	1.60	21.65	19.92	3.85	2.87	4.47
NO ₃23	6.21	2.75	trace
Ca	23.45	20.49	13.73	10.35	21.12	9.91	20.10
Mg	5.45	5.38	3.03	3.14	2.57	2.91	4.01
Na	4.77	8.33	14.78	19.75	1.94	4.84	3.04
K							
SiO ₂	4.99	7.04	3.83	3.04	18.80	45.27	6.47
Al ₂ O ₃ , Fe ₂ O ₃52	.38	.47	7.29	1.96
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Denudation factor....	105.	98.	22.7	46.2	53.	50.4	16.

These analyses tell a consistent story. The St. Lawrence represents a humid area, and every square mile of it contributes something to the salinity of the waters. Hence a solvent activity of 105 tons per square mile. The Mississippi is a blend of waters from humid regions on the east and arid or semi-arid plains to the west, and its load is, therefore, proportionately lowered. The Colorado and Rio Grande are typical of areas which are largely arid, and many square miles of their nominal drainage basins add nothing to the saline burdens. The Amazon and the Uruguay show the low salinity of the tropical forest regions, and the Nile flows for a thousand miles of its course through a desert. The saline matter of the Nile comes in great part from the regions south of Khartoum. It has no tributaries worth considering north of the Atbara.

Even on the purely chemical side the analyses are instructive. The water of the St. Lawrence is essentially a calcium carbonate solution; in the Colorado and Rio Grande sulphates and chlorides predominate, and calcium is relatively low; the Mississippi has an intermediate character. As a rule the waters from arid regions resemble the Colorado; those from humid areas are more like the St. Lawrence. This, of course, is not an absolute rule, but it holds fairly well in a broad general way. It is a distinct aid in discussing the larger problems of chemical denudation.

¹ See "Data of Geochemistry," Bull. 830 U. S. Geol. Surv., p. 75.

² *Ibid.*, p. 82.

³ Le Nil, l'Égypte, le Soudan. Paris, 1891.

In an essay of this kind it is impracticable to give all the details of the discussion. It is enough to indicate their nature briefly, for the results can only be approximations to the truth, with no claims to finality. Taking the several continents in order, the composition of their waters tributary to the ocean may be estimated as follows:

For the United States the data given by Dole and Stabler in Water-Supply Papers 234 and 236 are taken, together with those of Forbes and Skinner for the Colorado. The river basins considered are the St. Lawrence, Hudson, Delaware, Susquehanna, Potomac, James, Roanoke, Neuse, Cape Fear, Pedee, Santee, Savannah, Altamaha, Apalachicola, Alabama, Pearl, Mississippi, Brazos, Colorado of Texas, Rio Grande, Colorado of Arizona, and Sacramento.¹ Each average composition is roughly weighted proportionally to the total amount of dissolved matter transported by the river in a year, and in that way the mean for the United States is obtained; a mean which is not likely to be much altered by any future analyses. According to Dole and Stabler the quantity of saline matter carried from these basins is 87 short tons or about 79 metric tons per square mile annually.

For the rest of North America only an estimate is possible. Eleven analyses of river waters from the Saskatchewan system, one from the Yukon, and one from the Ottawa, give a mean composition of the dissolved matter resembling that of the St. Lawrence. So much for British North America and Alaska. For Mexican and Central American waters no data are at hand, but it is probable that they would be, for northern Mexico, at least, similar to those of Arizona, New Mexico and Texas. That is, the waters north of the United States and south of it would vary from the mean obtained for the United States, in opposite directions, and so tend to balance each other. In short, the average for the United States will probably represent fairly well the average for the entire continent. If we assume that six millions of square miles of North America lose 79 metric tons in solution per square mile per annum, and that the composition of the saline matter so transported is that found for the United States alone, we shall not be very far from the truth.

Analyses of South American river waters are not numerous. For the great rivers north of the Amazon I have found no data at all. We may assume, however, that they will resemble the Amazon in their general features, and taking the analysis and denudation factor of that river as typical, we can regard its composition as representing the waters of about three millions of square miles. Figures for the Uruguay, draining 151,000 square miles, I have already given. There is also an analysis by

¹ Average of 20 composite analyses of 10 daily samples each, furnished by Mr. R. B. Dole. Not in Dole's memoir.

Schoeller of water from the Rio Negro, which I assign equal weight with that of the Uruguay. The data for the River Plate are unsatisfactory, for the analyses suggest a strong probability of tidal contamination. South of the Plate the streams show a resemblance to those of our own southwestern areas, of which the Colorado is the type. I have averaged together twelve analyses, including two Chilean rivers, and so obtained the results given in the following table. In combining the analyses they are weighted as indicated at the foot of each column.

	<i>Amazon.</i>	<i>Uruguay.</i>	<i>Negro.</i>	<i>12 rivers.</i>	<i>Weighted mean.</i>
CO ₂	34.75	22.91	39.10	19.82	32.48
SO ₄	7.37	5.02	1.23	17.22	8.04
Cl	3.85	2.87	4.43	19.14	5.75
NO ₃	2.75	1.95	2.65	.62
Ca	21.12	9.91	17.82	10.77	18.92
Mg	2.57	2.91	1.96	2.82	2.59
Na	1.94	4.84	10.24	21.01	5.03
K	2.31	1.56	1.67	1.95
Fe ₂ O ₃ , Al ₂ O ₃	7.29	1.96	1.52	.36	5.74
SiO ₂	18.80	45.27	21.75	4.54	18.88
	100.00	100.00	100.00	100.00	100.00
Weight	12.	1.	1.	2.	

This mean I shall assume as representing the waters of four millions of square miles, with a denudation factor, as shown by the Amazon, Uruguay, and, for comparative purposes, the Colorado also, of 50 tons per square mile annually. This is only a rough estimate, but it is a probable one and the best I can make with the existing material. The Amazon dominates the combination, just as the Mississippi does in the United States. Data relative to the Magdalena, Orinoco, Demerara, San Francisco, and Plate, the latter at some point far above the possibility of tidal contamination, are much to be desired.

Analyses of European river waters are abundant, but rarely numerous enough for any one stream to give conclusive evidence as to its denudation value. I have, however, averaged together 300 analyses of European lakes and rivers,¹ first by groups and then weighting each group proportionally to its drainage area. In that way I have obtained a highly probable mean for the composition of the waters, which will appear in a table to be given later. The denudation factor I can only estimate roughly. According to Geikie² the Thames carries in solution past Kingston 548,230 British or 556,930 metric tons dissolved inorganic matter annually. The drainage area is 6100 square miles; hence a denudation factor of 91.3 tons; an estimate much lower than that of Reade. For the Meuse above Liège, the

¹ Not 300 rivers. Some streams, like the Elbe and Danube, are represented by numerous analyses.

² Text-book of Geology, 4th ed., vol. 1, p. 489.

figures published by Spring and Prost¹ give a factor of 139 tons per square mile. Reade's estimate for all Europe is 100 tons, and that seems to be fairly probable. For Europe, then, I shall assume that 3,000,000 of square miles suffer solvent denudation at the rate of 100 tons per mile, a figure which is much like that of the St. Lawrence. Europe is generally well-watered, and its waters have all the characteristics of those from the humid areas of the United States. In the latter the denudation factor is lowered by the arid regions of the southwest.

The African material is very scanty. In addition to the figures already cited for the Nile, with a drainage area estimated at 1,293,050 square miles, I have found only analyses of three small Algerian rivers which exhibit all the peculiarities of waters from other semi-arid districts. Ignoring the latter I shall estimate that 1,500,000 square miles in Africa are represented by the Nile with the denudation factor of 16 tons. I shall also assume that 6,500,000 square miles are fairly equivalent in character to South America, with the same composition of the waters and the same denudation factor of 50 tons. The desert regions, like the Sahara, of course count for nothing. Analyses of water from the Niger, Congo, Orange, and Zambesi are much needed.

The data relative to Asiatic waters are still more defective. I have found analyses by Schmidt of water from Lake Baikal and the river Om in Siberia, and one by Nicholson of the Mahanuddy in India. Waters of saline lakes, not tributary to the ocean, I of course leave out of account. The water of Lake Baikal is closely similar in character to that of the Yukon and St. Lawrence; that of the Mahanuddy more resembles the waters of tropical South America. With these feeble clues I can only make a very rough estimate for Asia, as follows: Assume three millions of square miles to average like Europe; three millions like the United States; and one million like South America. Large areas in Asia obviously are left out of consideration; the Caspian depression, the deserts of Central Asia, and the Arabian peninsula. The streams which reach the sea from Arabia are too insignificant to carry any weight in the general discussion. For Australia I have no data.

To sum up, the crude figures upon which to base further discussion are as follows, beginning with a summary of the denudation values for each continent:

North America	6,000,000 sq. miles, at 79 tons.....	474,000,000 tons
South America	4,000,000 " " " 50 "	200,000,000 "
Europe 3,000,000 " " " 100 "	300,000,000 "
Asia 7,000,000 " " " 84 "	588,000,000 "
Africa 8,000,000 " " " 44 "	352,000,000 "
Total	1,914,000,000 "

¹ Ann. Soc. Géol. Belg., vol. 11, p. 123.

The total area accounted for is 28,000,000 square miles, with a mean solvent denudation of 68.4 tons. The incompleteness of the figures is due to the fact that large areas of the earth's land surface either do not drain into the ocean, or, as in the cases of Arabia, the coast of Peru, etc., contribute little or nothing to it. There is, of course, local denudation in areas like the Great Basin of the United States and the Caspian depression; but that does not fall within the scope of the present discussion. Furthermore, the circumpolar regions such as Greenland and the Antarctic continent have no large rivers, and must be left out of account. The total land area to be considered, that is, the area which contributes to the salinity of the ocean, is, according to Murray, 39,697,400 square miles, or 40,000,000 in round numbers. Assuming that the figures so far given for 28,000,000 square miles represent a fair average, the total amount of saline matter carried into the ocean by the river drainage of the world is 2,735,000,000 metric tons, an estimate only a little more than half that given by Murray.

The composition of the saline matter thus carried into the ocean is given in the next table. The averages for Asia and Africa are made up in the manner already indicated: the final general mean roughly weights the individual means proportionally to the number of tons given in the last column of the foregoing table:

	<i>N. America.</i>	<i>S. America.</i>	<i>Europe.</i>	<i>Asia.</i>	<i>Africa.</i>	<i>General mean.</i>
CO ₂	33.40	32.48	39.98	36.61	32.75	35.15
SO ₄	15.31	8.04	11.97	13.03	8.67	12.14
Cl	7.44	5.75	3.44	5.30	5.66	5.68
NO ₂	1.15	.62	.90	.98	.58	.90
Ca	19.36	18.92	23.19	21.23	19.00	20.39
Mg	4.87	2.59	2.35	3.42	2.68	3.41
Na	9.23	5.03	4.32	6.42	4.90	6.40
K		1.95	2.75	1.54	2.35	1.51
R ₂ O64	5.74	2.40	1.96	5.52	2.75
SiO ₂	8.60	18.88	8.70	9.51	17.89	11.67
	100.00	100.00	100.00	100.00	100.00	100.00
Weight	10.	4.	6.	11.	7.	

The final mean, regardless of possible corrections, is curiously near the average figures for three great rivers, the Mississippi, Amazon, and Nile. It is probably rather high in silica, but on the whole it is as near to the truth as can be determined from the existing data. The greater rivers of Africa and Asia are yet to be studied, and much more should be done in South America. In the analyses reported by Dole, sodium and potassium are rarely discriminated, and hence the two radicles are given together as sodium alone. This error, however, is compensated by the excessive and evidently erroneous determinations of potassium in the Nile

and in some European rivers, so that the final figures are not far out of the way. Dr. Chase Palmer, working in co-operation with Dole in the study of American waters, made more than one hundred careful determinations of the ratio between sodium and potassium in over forty rivers, and found it to be very nearly 4.2 to 1. This ratio is practically identical with that given in my general mean, namely, 4.24 to 1, and the latter is, therefore, satisfactory.

In order to apply the foregoing averages to the discussion of either chemical denudation or geological time, certain other data are needed. Some of these are general, others are of the nature of minor corrections. Professor J. Joly,¹ in order to determine the age of the ocean, divided its total content of sodium by the amount annually carried into it by rivers, and so deduced an uncorrected value of 97,600,000 years. The computation is simple enough, and is based upon the fact that sodium is less removed from the waters than other substances; if, indeed, it is appreciably removed at all. Calcium and magnesium are precipitated as carbonates; potassium is absorbed by clays, silica goes to form siliceous oozes. Sodium alone, among the basic elements, tends to accumulate in the ocean with little loss, and so to give some indication of its geological age.

Joly, however, employed data of a defective character. Murray's estimate of the sodium in rivers was taken, which, as we have seen, needs serious modification. For the volume of the ocean he combined Wagner's, or rather Karstens', estimate of its area with Murray's figure for its average depth, and used Dittmar's analyses for the proportion of sodium in it. The last datum is satisfactory; the others need revision.

The best estimate of the volume of the ocean is probably that of Karstens,² 1,285,935,211 cubic kilometers. This, with Murray's figure for the mean density, 1.026, gives the ocean a mass of $1,319,650 \times 10^{12}$ metric tons. Assuming an average salinity of 3.5 per cent., the total saline matter in the ocean amounts to $46,188 \times 10^{12}$ tons; which, according to Dittmar's analyses, is distributed as follows:

	<i>Per cent.</i>	<i>Metric tons $\times 10^{12}$.</i>
Cl	55.292	25,538.
Br188	86.8
SO ₄	7.692	3,553.
CO ₂207	95.6
Na	30.593	14,130.
K	1.106	510.8
Ca	1.197	552.8
Mg	3.725	1,721.
	100.000	46,188.0

The small traces of other substances in the ocean only represent insignificant corrections to these figures.

¹ Trans. Roy. Soc. Dublin (2), vol. 7, p. 23, 1899. Rep. British Asso. Adv. Sci., 1900, p. 369.

² Eine neue Berechnung der mittleren Tiefen der Ozeane. Inaug. Diss., Kiel, 1894.

From the figures previously given, for the average composition of river waters and the total chemical denudation of the globe, 175,040,000 metric tons of sodium are annually discharged into the sea. The crude quotient,

$$\frac{\text{Na in ocean}}{\text{Na in rivers}} = 80,726,000;$$

the time in years needed to furnish the entire amount of marine sodium; assuming a sodium-free ocean at the start and a uniform rate of supply throughout all geological time. Any probable change in either of these assumptions will reduce the quotient, although other considerations may tend to increase it. The first correction to be examined operates in the latter direction.

A part of the sodium found in the discharge of rivers is the so-called "cyclic sodium"; that is, sodium in the form of salt lifted from the sea as spray and blown inland to return again to its source in the drainage from the land. Near the sea coast this cyclic salt is abundant; inland its quantity is small. For example, by careful analyses of rainfall, continued over long periods of time, the following amounts of cyclic salt have been determined. The figures represent pounds per acre per annum of sodium chloride.

<i>Locality.</i>	<i>NaCl in rain.</i>
Rothamsted, England.....	24.
Cirencester, England.....	36.1
Perugia, Italy.....	37.95
Barbados	193.

In central Massachusetts, according to Mrs. Ellen S. Richards,¹ the cyclic salt, at distances of 50 to 100 miles from the coast, amounts to 23.2 pounds per acre per annum.

The Rothamsted figures are very suggestive. Rothamsted lies in the Thames valley, and if its figure for sodium chloride in rain be taken as a fair average for the entire drainage basin, 6100 square miles, the quantity there brought down amounts to 41,732 British tons annually, or 16,445 tons reckoned as sodium alone. Analyses of the Thames give sodium as 3.26 per cent of the total inorganic matter in solution, or, in terms of the discharge already cited, 17,872 tons. Here the cyclic sodium is nearly as much as the total amount carried by the stream; but of course one cannot assume that all of the cyclic portion finds its way back to the ocean in any brief or relatively brief time. It is enough to say that in the British islands the correction for cyclic salt must be large; while for the great continental rivers like the Mississippi, St. Lawrence, Amazon, Danube, or Nile it is very much smaller.

¹ Private communication. For the other figures, see Data of Geochemistry, p. 47.

It is difficult, with existing data, to evaluate the correction for cyclic sodium with any great approach to accuracy. It probably varies for different regions, but from the well-known "chlorine maps" of New England and New York, with their "isochlors," a good estimate for the United States can be made. This part of the work has been done by Dr. Becker, whose discussion of the subject appears elsewhere. Another, cruder estimate may be made as follows: If we assume with regard to the United States that the salt brought down in rain is represented by the Rothamsted figures for a strip 100 miles wide following the coast line, an area, roughly, of about 450,000 square miles, the quantity of sodium thus found amounts to 1,231,300 metric tons. Regarding the correction for the interior of the United States as zero, an assumption which is justified by a study of the isochlors, the final result may be obtained as follows: The total sodium carried by the rivers of the United States to the sea, after correcting the crude value already given in the table of analyses by Palmer's value for the Na-K ratio, amounts to, roughly, 17,500,000 tons. The cyclic sodium is only 7 per cent. of the latter quantity, whereas Joly allows 10 per cent., but the smaller figure is probably a maximum. Subtracting 7 per cent. from the total sodium carried by the rivers, 175,040,000 metric tons per annum, the remainder is 162,787,200 tons; which, divided into the sodium of the ocean gives a quotient of 86,800,000 years. Joly's correction of 10 per cent. is very nearly equivalent to the assumption that the entire run-off of the globe, 6524 cubic miles, according to Murray, carries on an average one part per million of chlorine. The chlorine maps, so far as they have been made, show this figure to be excessive.

The foregoing correction for "cyclic salt" is, however, not final. It has already been suggested that the wind-borne salt is only in part restored to the ocean, at least within reasonable time. Some of it is retained by the soil, if not permanently, at least rather tenaciously; and the portion which falls into depressions of the land may remain undisturbed almost indefinitely. In arid regions, like the coasts of Peru, Arabia, and parts of western Africa, a large quantity of cyclic salt must be so retained in hollows or valleys which do not drain into the sea. Torrential rains, which occur at rare intervals, may return a part of it to the ocean, but not all. Some writers, like Ackroyd¹ for example, have attributed the saline matter of the Dead Sea to an accumulation of wind-borne salt; an assumption which contains elements of truth, but is probably extreme. A more definite, but equally striking instance of the sort is furnished by the Sambhar salt lake in northern India, as studied by Holland and Christie.² This lake, situated in an enclosed drainage basin of 2200 square miles and

¹ Chem. News, vol. 89, p. 18, 1904.

² Records Geol. Survey India, vol. 36, p. 154, 1909.

over 400 miles inland, appears to receive the greater part, if not all of its salt from dust-laden winds which, during the four hot, dry months, sweep over the plains between it and the arm of the sea known as the Rann of Cutch. Analyses of the air during the dry season, showed a quantity of salt so carried which amounted to at least 3000 metric tons over the Sambhar lake annually, and 130,000 tons into Rajputana. These quantities are sufficient to account for the accumulated salt of the lake, which the authors were unable to explain in any other way.

Examples like this of the Sambhar lake are of course exceptional. In a rainy region salt dust is quickly dissolved and carried away in the drainage. Only in a dry period can it be transported as dust from its original point of deposition to points much further inland. It appears, however, that some salt is so withdrawn, at least for an indefinitely long time, from the normal circulation, and should, if it could be estimated, be added to the amount now in the ocean. Such a correction, however, would doubtless be quite trivial, and, therefore, negligible; and the same remark must apply to all the visible accumulations of rock salt, like those of the Stassfurt region, which were once laid down by the evaporation of sea water. The saline matter of the ocean, if concentrated, would represent a volume of over 4,800,000 cubic miles; a quantity compared with which all beds of rock salt become insignificant.

But although the visible accumulations of salt are relatively insignificant, it is possible that there may be quantities of disseminated salt which are not so. The sedimentary rocks of marine origin must contain, in the aggregate, vast amounts of saline matter, widely distributed, but rarely determined by analysis. These sediments, laid down from the sea, cannot have been completely freed from adherent salts, which, insignificant in a single ton of rock, must be quite appreciable when cubic miles are considered. The fact that their presence is not shown in ordinary analyses merely means that they were not sought for. Published analyses, whether of rocks or of waters, are rarely complete, especially with regard to those substances which may be said to occur in "traces."

It is perhaps not possible to estimate the quantity of this disseminated salt, and yet a maximum limit may be assigned to it. In a former publication¹ it was shown that 84,300,000 cubic miles of the average igneous rock would, upon decomposition, yield all the sodium of the ocean and the sedimentaries. This estimate involved the maximum, not the mean salinity of the ocean, and also a different value for the mass of the latter from that now adopted. In order to revise the estimate, which must be considerably reduced, it is desirable first to consider the average composition of the two classes of rocks, especially since the data are applicable to other phases of the discussion than that now under consideration.

¹ *Data of Geochemistry*, pp. 28-29.

For the average composition of the igneous rocks there are two principal estimates: Clarke's,¹ based upon analyses made in the laboratories of the United States Geological Survey alone, and Washington's,² which includes analyses from all parts of the world. These two composites, reduced to 100 per cent. and condensed by union of minor and unimportant constituents, assume the following form:

	<i>Clarke.</i>	<i>Washington.</i>	<i>Mean.</i>
SiO ₂	59.99	57.78	58.88
Al ₂ O ₃	15.04	15.67	15.36
Fe ₂ O ₃	2.59	3.31	2.95
FeO	3.34	3.84	3.59
MgO	3.89	3.81	3.85
CaO	4.81	5.18	4.99
Na ₂ O	3.41	3.88	3.65
K ₂ O	2.95	3.13	3.04
H ₂ O	1.92	1.78	1.85
Minor constituents..	2.06	1.62	1.84
	100.00	100.00	100.00

In the mean the Survey analyses, of which many are included in Washington's average, evidently receive double weight.

When the average igneous rock decomposes, it loses some substances by leaching, and gains others, such as oxygen, water, and carbon dioxide. The products of decomposition, as nearly as can be estimated, are 5 per cent. limestones, 15 per cent. sandstones, and 80 per cent. the residues which consolidate to form slates and shales. The composite analyses of sedimentary rocks, made in the laboratory of the United States Geological Survey,³ are given in the next table, with their weighted average recalculated to 100 per cent.

	<i>Shales.</i>	<i>Sandstones.</i>	<i>Limestones.</i>	<i>Weighted mean.</i>
SiO ₂	58.38	78.66	5.19	58.51
Al ₂ O ₃	15.47	4.78	.81	13.07
Fe ₂ O ₃	4.03	1.08	.54	3.40
FeO	2.46	.30	2.00
MgO	2.45	1.17	7.90	2.52
CaO	3.12	5.52	42.61	5.42
Na ₂ O	1.31	.45	.05	1.12
K ₂ O	3.25	1.32	.33	2.80
H ₂ O	5.02	1.64	.77	4.28
CO ₂	2.64	5.04	41.58	4.93
Minor constituents.....	2.33	.45	.31	1.95
	100.46	100.41	100.09	100.00
Weight	80.	15.	5.	

¹ U. S. Geol. Surv., Bull. 419, pp. 4-9, 1910.

² U. S. Geol. Surv. Bull. 419, p. 10.

³ U. S. Geol. Surv. Prof. Paper, No. 14, p. 106, 1908.

In the ocean, as previously shown, there are 14130×10^{12} metric tons of sodium. This amount would be supplied by the *complete* decomposition of 48,225,000 cubic miles of an igneous rock having the composition shown by Clarke's average, or 42,385,000 cubic miles on the basis of Washington's figures. Some sodium, however, is retained by the sedimentary rocks, for the reason that decomposition is rarely, if ever, perfect. Fragments or particles of feldspar are especially common in the sedimentaries. On comparing the average composition of the latter with that of the igneous rocks, assuming that alumina has remained constant, the following ratios appear:

	Clarke.	Washington.
Na ₂ O retained, per cent.....	1.29	1.38
Na ₂ O lost, per cent.....	2.12	2.50
	<hr style="width: 50px; margin: 0 auto;"/>	<hr style="width: 50px; margin: 0 auto;"/>
	3.41	3.88

Hence, for the total volume of igneous rock needed to furnish all the sodium of the ocean and of the sediments, assuming that the sodium lost represents the marine portion, we have:

From Clarke's average.....	77,570,000 cubic miles
From Washington's average.	65,782,000 " "

These figures correspond, respectively, to a shell of igneous rock, completely enveloping the globe, 2050 feet thick in one case, or 1740 in the other. For present purposes the higher estimate will be taken, in order that the deductions may be maxima.

If, now, the sedimentary rocks were of the same volume as the igneous rocks from which they were derived, and if the sandstones form 15 per cent. of the 77,570,000 cubic miles, the bulk of the latter will be, very roughly, 10,635,500 cubic miles. The assumptions thus made are of course not exact, but they will suffice for the computations now in hand. The errors are negligible, so far as present needs are concerned. Assume further that the sandstones, the most porous of the rocks, contain an average pore space of 20 per cent., or 2,127,100 cubic miles, and that all of it was once filled by sea water, representing 99,861,000,000 metric tons of sodium. If all of that sodium were now present in the sandstones, and erosion began at the rate now assigned to the rivers, namely, 175,040,000 tons of sodium annually, the entire accumulation would be removed in 570,000 years. This, compared with the estimate already reached for geological time, is an almost negligible quantity. Even if the entire volume of the sedimentary rocks carried the same proportion of sodium as is here assigned to the sandstones, it would be exhausted in about 3,800,000 years. The correction for disseminated salt is, therefore, in all probability small, and not likely to exceed 1 per cent.

The foregoing calculations, so far as geologic time is concerned, imply the assumption that rivers add sodium to the sea at an average uniform rate, slight accelerations being offset by small temporary retardations. This subject is to be discussed by Mr. G. F. Becker; but one phase of it demands consideration here. The present rate of discharge has been hastened during modern times by human agency, and that acceleration may be important to take into account. The sewage of cities, the refuse of chemical manufactures, etc., is poured into the ocean, and so disturbs the rate of accumulation of sodium quite perceptibly. The change due to chemical industries, so far as it is measurable, is wholly modern, and that due to human excretions is limited to the time since man first appeared upon the earth. Its exact magnitude, of course, cannot be determined; but its order seems to be measurable, as follows:

According to the best estimates, about 14,500,000 metric tons of common salt are annually produced, equivalent to 5,700,000 tons of sodium. If all of that was annually returned to the ocean, it would amount to a correction of about 3.25 per cent. on the total addition of sodium to the sea. The fact that much of it came directly or indirectly from the ocean in the first place is immaterial to the present discussion; the rate of discharge is affected. All of this sodium, however, is not returned; much of it is permanently fixed in manufactured articles. The total may be larger, because of other additions, excretory in great part, which cannot be estimated; but we may assume, nevertheless, a maximum of 3 per cent. as the correction to be applied. Allowing 7 per cent., as already determined, to cyclic or wind-borne sodium, and 1 per cent. to disseminated salt of marine origin, the total correction is 11 per cent. This reduces the 175,040,000 tons of river sodium to 155,785,600 tons, and the quotient representing crude geologic time becomes 90,700,000 years.

The corrections so far considered are all in one direction, and increase, by a roughly evaluated amount, the apparent age of the ocean. Other corrections, whose magnitudes are more uncertain, tend to compensate the former group. The ocean may have contained primitive sodium, over and above that since contributed by rivers. It receives some sodium from the decomposition of rocks by marine erosion, which is estimated by Joly to be a correction of less than 6 per cent. and more than 3 per cent. on the value assigned to geologic time. Sodium is also derived from volcanic ejectamenta, from "juvenile" waters, and possibly from submarine rivers and springs. The last possibility has been considered by Sollas,¹ but no numerical correction can be devised for it. These four sources of sodium in the sea may be grouped together as non-fluviatile, and reduce the numerator of the fraction which gives the age of the ocean. Whether

¹ Presidential address, Quar. Journ. Geol. Soc., May, 1909.

they exceed, balance, or only in part compensate the other corrections it is impossible to say. The rough quotient at first obtained, 80,726,000 years, is as probable as any other value that might be chosen. That value, as will be shown by Mr. Becker's calculations, is certainly a maximum. It represents, in its essential features, Joly's method of computing the age of the ocean, but takes, with one minor exception, no account of changes of rate in the annual additions to the marine salinity. Joly's final estimate of the age is 90,000,000 years, with a possible increase of 6 per cent. due to a revision of the mass of the ocean.

Reade, in the investigation cited at the beginning of this paper, estimated the solvent denudation of England and Wales at 143.5 British, or 146 metric tons per square mile per annum, or one foot in 12,978 years. The smaller denudation factors now found lead to different results. For the United States, excluding the Great Basin, the factor of 79 tons gives, for a lowering of one foot, 23,948 years. For South America the figures are 50 tons and 37,751 years; for Europe, 100 tons and 18,875 years and for the Nile Valley, 16 tons and 93,924 years. For the 40,000,000 square miles of the globe, which drain into the ocean, the average values are 68.4 tons and 27,660 years, estimates that are subject to large corrections, which Reade did not take into consideration. The foregoing figures only apply to his method of computation.

On critical examination of the data it is clear that the total apparent amount of solvent denudation is not a true measure of rock decomposition. In the general mean of all the river analyses now under discussion, 0.90 per cent. of NO_3 and 35.15 per cent. of CO_2 appear. The NO_3 came entirely or practically so from atmospheric sources; the CO_2 was derived partly from the atmosphere and partly from the solution of limestones. Dealing now only with the existing discharge of rivers, we must subtract these atmospheric additions from the total annual load of dissolved inorganic matter, before we can compute the real amount of rock denudation.

The land surface of the earth is covered, nearly enough for present purposes, by 75 per cent. of sedimentary and 25 per cent. igneous and crystalline rocks;¹ and it is on or near this surface that the flowing waters act. The limestones, as shown in my former discussion, constitute only one-twentieth of the sediments, or 3.75 per cent. of the entire area; but the proportion of carbonates derived from them must be very much larger. The composite and average analyses of rocks give, for lime, 4.81 per cent. in the igneous, and 5.42 in all the sedimentaries, equivalent to 3.78 and 4.26 per cent. of CO_2 respectively. Assuming that all the surface rocks yield lime at an equal rate, which is obviously not quite true, and multiplying these figures by the areas represented as 1 to 3, the

¹ Estimate by A. von Tilló, actually 75.7 and 24.3.

relative proportions of the CO_2 radicle become 3.78:12.78, or 1:3.4 nearly. The last figure should be higher, because of the more rapid solution of the limestones, but if we accept the ratio as it stands we may use it to determine the approximate proportions of the CO_2 radicle derived from limestones and from the atmosphere acting upon crystalline rocks. On this basis, 8 per cent. of CO_2 should be deducted from the percentage in the river waters, together with the 0.9 per cent. of NO_2 . Making the subtraction from the total river load of dissolved matter, 2,735,000,000 tons, there remains 2,491,585,000 tons, or about 62.3 tons per square mile on the average, for the 40,000,000 of square miles of land which are assumed to drain into the ocean. This implies a lowering of the land by solvent denudation at the rate of one foot in 29,941 years, or 30,000 in round numbers. The last estimate may be subject to large future corrections, but probably it is correct to within 10 per cent.

It is possible, with the data now in hand, to take still another step and determine approximately the quantity of *chemical* sediments annually precipitated in the ocean. For this purpose we may first, knowing the average composition of river waters, and also their total load of dissolved inorganic matter, compute the actual amount of each radicle poured into the ocean in one year. The total amount so added is 2,735,000,000 metric tons, distributed as follows:

CO_2	961,350,000 tons
SO_4	332,030,000 "
Cl	155,350,000 "
NO_2	24,614,000 "
Ca	557,670,000 "
Mg	93,264,000 "
Na	175,040,000 "
K	41,299,000 "
R_2O_3	75,213,000 "
SiO_2	319,170,000 "
	2,735,000,000 "

If, from each of these quantities we subtract the amount annually retained in solution by the sea, the difference will represent the amount precipitated. To do this, an assumption must be made as to the age of the ocean; but whatever probable figure is thus assumed, the results will be of the same order of magnitude. For example, the ocean contains 552.8×10^{12} metric tons of dissolved calcium, which quantity, divided by the assumed age, gives the annual increment. If the age of the ocean is 100,000,000 years, the annual addition of calcium is 5,528,000 tons; if only 50,000,000 years it is 11,056,000 tons. Subtracting these quantities from the total calcium of the river waters the remainders become 552,142,000 and 546,614,000 tons respectively, the difference being much less

than the actual uncertainties of the computation. If, for the sake of uniformity, we take as the crude age of the ocean the quotient first obtained, 80,726,000 years, the chemical precipitates are represented by the following annual quantities:

SO ₄	288,017,000	metric tons
Ca	550,822,000	" "
Mg	71,945,000	" "
K	34,971,400	" "
R ₂ O ₃	75,213,000	" "
SiO ₂	319,170,000	" "

Combined, the radicles thus precipitated in the ocean, yield the following substances:

Gypsum, CaSO ₄ .2H ₂ O.....	516,020,000	metric tons
Calcium carbonate, CaCO ₃ ..	1,077,030,000	" "
Magnesium carbonate, MgCO ₃	249,587,000	" "
Limonite, ¹ 2 Fe ₂ O ₃ .3H ₂ O..	87,505,000	" "
Silica, SiO ₂	319,170,000	" "

The potassium remains unaccounted for. Part of it is taken up by the clay-like substances in the oceanic silts, and part goes to form glauconite; but it is not worth while to speculate upon the relative proportions of potassium withdrawn by these two processes from solution.

The figures given above for the quantities of the five chemical precipitates annually deposited in the ocean can, of course, make no pretense to accuracy. They are merely rough approximations to the truth, but they tell something of the relative magnitudes. Even if we knew precisely the age of the ocean, it would not be practicable to reckon backward and so to determine the total mass of deposits formed during geological time. The figures tell us what is happening to-day, but are inapplicable to the past. The reason for this statement is, that apparently the different deposits have formed at different rates. In the beginning of chemical erosion fresh rocks were attacked, and relatively more silica and less lime passed into solution. At present, limestones, laid down in previous geologic ages, are being dissolved, and calcium is added to the ocean more rapidly than in pre-Cambrian times. This is not mere speculation. A study of river waters with reference to their origin, whether from crystalline or sedimentary rocks, fully justifies my assertions.

The vexed question as to the source of oceanic chlorine, I have so far left out of consideration. Dr. Becker has shown that volcanic agencies are adequate to account for it. Some, however, may have come from ferrous chloride, lawrencite, a compound which is common in meteoric irons. If our planet is analogous to a great meteorite, lawrencite must

¹ Assuming R₂O₃ to be all Fe₂O₃. It is certainly, in part, Al₂O₃.

exist in it, and was possibly, in early geologic periods, leached into the ocean in large amounts. Its iron would be precipitated by the alkaline carbonates of river waters, while chlorides of the alkaline metals were produced. Dr. Becker, however, inclines to regard deeply buried lawrencite as the origin of volcanic chlorine, and it is possible that the great mass of this ferrous chloride underlay the specifically lighter primeval rocks. It is also conceivable that the earliest crystalline rocks were richer in easily decomposable minerals like sodalite than the surface rocks of to-day, and, therefore, added more chlorine to the ocean than is leached into it now. Such rocks, if they existed, would be more rapidly eroded than the less soluble species, and, consequently, less abundant at the present time. A primitive atmosphere, rich in chlorine, and an ocean of weak hydrochloric acid may have once existed, but their assumption is by no means necessary in order to account for the known facts.

This memoir is entitled "A Preliminary Study of Chemical Denudation." It has been written in order to make existing data more available for discussion, and to point out the deficiencies in our knowledge. If it stimulates investigation; if it leads others to the examination of the greater Asiatic, African, South American and Australian rivers, or to more extended studies of the chemistry of rainfall, its main purpose will be fulfilled. The assumptions which it is now necessary to make ought to be replaced by definite evidence of a sort which is easily obtainable.¹

¹ Published by permission of the Director of the United States Geological Survey. Becker's memoir, to which references have been made, appears simultaneously with this paper.







